

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY, UNIVERSITY OF NOTRE DAME, NOTRE DAME, IND.]

Photoionization and  $\gamma$ -Induced Oxidation of Aromatic Amines in Rigid Organic Glasses<sup>1</sup>

BY M. KONDO, M. R. RONAYNE, J. P. GUARINO, AND W. H. HAMILL

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Photoionization of *N,N*-dimethyl-*p*-phenylenediamine occurs in polar glasses at 77°K. but not in pure hydrocarbons. Addition of electron-accepting solutes greatly enhances photoionization yields in polar glasses, but only the more easily reduced of these enhance yields in nonpolar glasses.  $\gamma$ -Irradiation produces much higher yields of amine cation in nonpolar glasses than in polar glasses. In both types of media yields can be enhanced by addition of electron acceptors, but yields are much smaller in polar glasses. Results of  $\gamma$ -irradiation indicate that charge transfer is very largely responsible for amine cation yields.

## Introduction

Previous work<sup>2,3</sup> has demonstrated the importance of electron attachment and solvation in  $\gamma$ -irradiated organic glasses and provided indirect evidence that the primary cation can undergo either charge exchange or ion-molecule reactions. Charge exchange tends to decrease ion pair yields through charge migration and recombination, while ion-molecule reactions prevent positive charge exchange and promote stabilization of ion pairs, as do solutes of low ionization potential.

It is desirable to study positive charge exchange and ion recombination in  $\gamma$ -irradiated rigid media with authentic cations. Certain aromatic amines are eminently suitable for this purpose since they can be oxidized chemically, are readily photoionized, and the resulting free radical cations have distinctive optical absorption spectra and large extinction coefficients.<sup>4,5</sup>

When low concentrations of appropriate solutes are  $\gamma$ -irradiated in glasses, there are two possible mechanisms for the production of solute cations. One mechanism involves exchange of positive charge between an ionized solvent molecule and the solute. Another mechanism involves transfer of electronic excitation energy from solvent to solute. In this work energy transfer would be followed by the oxidation of amine. The mechanism of oxidation by energy transfer closely resembles direct photoionization and therefore a concurrent study of the photochemistry and radiation chemistry of these aromatic amines in rigid media was undertaken to demonstrate similarities and differences. In this work aromatic amines which had been studied previously were chosen according to their ease of photoionization and their solubilities in appropriate glasses.

## Experimental

Amines included Eastman White Label grade *N,N*-dimethyl-*p*-phenylenediamine (DMPD), *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD), triphenylamine (TPA), and *N*-methyl-diphenylamine (MDPA).

The phenylenediamines can be photoionized in Pyrex cells and were therefore used for all photochemical experiments. Their low solubility in hydrocarbon glasses rendered them unsuitable for  $\gamma$ -irradiation which requires appreciable concentrations of solute for cation formation. Many other solutes were sparingly soluble in hydrocarbons at  $-196^\circ$ ; consequently, direct comparisons between polar and nonpolar media are often, of necessity, only qualitative.

(1) The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission.

(2) M. R. Ronayne, J. P. Guarino, and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 4230 (1962).

(3) J. P. Guarino, M. R. Ronayne, and W. H. Hamill, *Radiation Res.*, **17**, 379 (1962).

(4) L. Michaelis, M. P. Schubert, and S. Granick, *J. Am. Chem. Soc.*, **61**, 1981 (1939).

(5) G. N. Lewis and D. Lipkin, *ibid.*, **64**, 2801 (1942).

Glassing solvents included: 2-methyltetrahydrofuran (MTHF), 3-methylpentane (3MP), 2-methylpentene-1 (2MP-1), 40% ether-50% 1-pentane-10% ethanol (EPA), 40% methylcyclohexane-60% isopentane (M<sub>2</sub>P<sub>3</sub>), and 40% ether-40% isopentane-20% triethylamine (EPT) described previously.<sup>2</sup> The phenylenediamines are oxidized by air but stock solutions of DMPD in 3MP were decolorized with charcoal and immediately introduced into cells and evacuated. Dilution, or change of solvent, was performed under vacuum, the cell sealed, and the concentration of amine determined by spectrophotometry.

Photolyses were performed with a high pressure mercury lamp (G.E. AH-6). In Pyrex cells only light of *ca.* 320 m $\mu$  could be absorbed by the amine. Doses for  $\gamma$ -irradiation were typically  $6.5 \times 10^{18}$  e.v./g.

## Results

**Preparation of Wurster's Red by Bromine Oxidation and by Photooxidation of DMPD.**—A solution of DMPD in methylcyclohexane was flushed with nitrogen gas and a dilute solution of bromine in methylcyclohexane was added. The green salt which precipitated was collected in air, toward which it appears to be fairly stable. As a precaution, samples for chemical analysis<sup>6</sup> were sealed *in vacuo*. Ethyl bromide was added to a similar sample of DMPD in methylcyclohexane and the air-free solution was photolyzed at room temperature. The precipitate which formed was collected and analyzed.<sup>6</sup> The results, relative to C<sub>8</sub>H<sub>12</sub>N<sub>2</sub>Br, were

| Anal. for | Chemical oxidation | Photooxidation | Theory |
|-----------|--------------------|----------------|--------|
| C         | 43.1               | 44.6           | 44.0   |
| H         | 5.9                | 5.3            | 5.6    |
| N         | 12.2               | 9.2            | 13.0   |
| Br        | 37.8               | 25.4           | 37.0   |

Portions of these salts were dissolved in water exposed to air; absorption maxima appeared at 520 and 560 m $\mu$  in both cases. This spectrum was stable for several minutes, as found previously,<sup>4</sup> and served to verify oxidation of DMPD in later experiments. It is clear that the photochemically prepared material contains some of the free radical bromide, but that it also contains other products which were not identified. The absorption spectra obtained by photo- and  $\gamma$ -oxidation of DMPD and TMPD in glasses were slightly shifted from those appearing in aqueous solutions of chemically oxidized amines.<sup>4,7</sup> Various data of interest appear in Table I.

**Photolyses at  $-196^\circ$ .** (a).—Photolysis of 0.3 mole % DMPD in MTHF for 2 min. produced DMPD<sup>+</sup> together with a relatively small yield of solvated electrons (e<sub>s</sub><sup>-</sup>).<sup>2</sup> The O.D.<sub>575</sub> of DMPD<sup>+</sup> was 1.39 and

(6) Midwest Microlab, Inc.

(7) W. C. Meyer and A. C. Albrecht, *J. Phys. Chem.*, **66**, 1168 (1962).

(8) The experiments described in (a)–(d) were performed with reproducible geometry.

TABLE I  
 SUMMARY OF DATA FOR AMINE CATIONS

| Cation  | $\lambda_{\max}$ , m $\mu$ | $\epsilon$ , l./mole cm. | Medium  | Method of prepn. | Lit.      |
|---|----------------------------|--------------------------|---|------------------|-----------|
| N,N-Dimethyl- <i>p</i> -phenylenediamine          | 515                        |                          | Aqueous   | Chem.            | Ref. 4    |
|   | 550                        | $6.5 \times 10^3$        | Aqueous   | Chem.            | Ref. 4    |
|   | 525                        |                          | MTHF, $-196^\circ$                                | Photo., $\gamma$ | This work |
|   | 575                        |                          | MTHF, $-196^\circ$                                | Photo., $\gamma$ | This work |
|   | 525                        |                          | 3MP, $-196^\circ$                                 | Photo.           | This work |
|   | 575                        |                          | 3MP, $-196^\circ$                                 | Photo.           | This work |
| N,N,N',N'-Tetramethyl- <i>p</i> -phenylenediamine | 560                        |                          | Aqueous   | Chem.            | Ref. 4    |
|   | 606                        | $1.1 \times 10^4$        | Aqueous   | Chem.            | Ref. 4    |
|   | 575                        |                          | 3MP, $-196^\circ$                                 | Photo.           | Ref. 7    |
|   | 635                        | $2 \times 10^4$          | 3MP, $-196^\circ$                                 | Photo.           | Ref. 7    |
| Triphenylamine                                    | 570, 656                   |                          | EPA, $-196^\circ$                                 | Photo.           | Ref. 5    |
|   | 560, 640                   |                          | MTHF, 3MP, $-196^\circ$                           | $\gamma$         | This work |
| Methyldiphenylamine                               | 635                        |                          | EPA, $-196^\circ$                                 | Photo.           | Ref. 5    |
|   | 650                        |                          | M <sub>2</sub> P <sub>3</sub> , EPA, $-196^\circ$ | $\gamma$         | This work |

that of  $e_s^-$  at 1200 m $\mu$  in MTHF was 0.40. Complete optical bleaching of the  $e_s^-$  band with Corning filter no. 2600, transmitting 750–1000 m $\mu$ , decreased O.D.<sub>575</sub> to 1.29. The extinction coefficient<sup>1</sup> of DMPD<sup>+</sup> is  $6.5 \times 10^3$ . That for  $e_s^-$  is estimated to be  $1.4 \times 10^4$  l./mole cm. assuming  $G(e_s^-)$  in pure MTHF equal to the limiting yield of naphthalenide ion at 0.3 mole % naphthalene in MTHF.<sup>3</sup> The concentrations of DMPD<sup>+</sup> and  $e_s^-$  are then 2.2 and  $0.3 \times 10^{-4}$  M. For reasons not known, the optical characteristics of these electrons differ from those trapped in  $\gamma$ -irradiated glasses. Warming the sample to room temperature removed all absorption; no permanent products appeared.

(b).—Photolysis of 0.3 mole % DMPD in MTHF with 2 mole % carbon tetrachloride or 2-propyl chloride for 2 min. gave O.D.<sub>575</sub> 3.6 in both cases and no  $e_s^-$  absorption. A green precipitate formed upon warming these glasses. When it was dissolved in water the spectrum coincided with that for the DMPD<sup>+</sup> salt formed by bromine oxidation.

(c).—It appears likely that organic halides undergo dissociative reduction by acting as electron acceptors. To verify this possibility, benzyl chloride was used as an electron acceptor since the spectrum of the benzyl radical is well known ( $\lambda_{\max}$  320 m $\mu$ ). Photolysis of  $3 \times 10^{-3}$  mole % DMPD and 2 mole % benzyl chloride in MTHF for 30 sec. gave an O.D.<sub>575</sub> 0.9 for DMPD<sup>+</sup> together with the spectrum of the benzyl radical; the O.D.<sub>320</sub> was *ca.* 0.65. Warming this solution to room temperature yielded the green precipitate.

(d).—Photolysis of  $7 \times 10^{-3}$  mole % DMPD in 3MP or 0.04 mole % DMPD in 2MP-1 for 4 min. gave no measurable yields of cation. Addition of 2 mole % 2-propyl chloride to DMPD in 3MP also produced no cation on photolysis. However, addition of 2 mole % carbon tetrachloride to  $7 \times 10^{-3}$  mole % DMPD in 3MP gave O.D.<sub>575</sub> 0.92 after photolysis for 2 min. Adding 0.1 mole % benzyl chloride in 3MP to DMPD gave neither DMPD<sup>+</sup> nor benzyl radicals by photolysis. The limited solubility of benzyl chloride precluded tests at higher concentrations.

Several other experiments were performed with a different geometry. Photolysis of 0.01 mole % DMPD in MTHF with added biphenyl or benzophenone produced spectra of the amine cation and of the anion of the second solute. With 0.1 mole % biphenyl present, the O.D.<sub>575</sub> of DMPD<sup>+</sup> was 0.30 and O.D.<sub>410</sub> of  $(C_6H_5)_2^-$  was 0.88, or  $4.6 \times 10^{-5}$  M for

cation and  $2 \times 10^{-5}$  M for anion. Optical bleaching was impossible; both spectra disappeared on warming and no permanent product formed. With benzophenone present,  $\lambda_{\max}$  for benzophenone anion appeared at 820 m $\mu$ , as in  $\gamma$ -irradiation, which corresponds to a large red shift from the absorption maximum for the anion prepared with sodium in MTHF at 77°K. for which  $\lambda_{\max}$  was 670 m $\mu$ .<sup>2</sup> The addition of biphenyl to DMPD in 3MP did not induce photoionization, nor was the biphenyl anion produced.

Photolysis of DMPD alone in ethanol yielded DMPD<sup>+</sup>; added biphenyl had no effect. Also, DMPD is not photoionized in 3MP alone, but 7 mole % butanol promotes photoionization.

Other preliminary tests on samples exposed to air showed that carbon tetrachloride, bromoform, carbon tetrabromide, and chloroform enhanced photoionization of DMPD and TMPD in hydrocarbon glasses. Ethyl iodide, methyl iodide, and bromobenzene had no evident effect. In 3 parts isopentane with 1 part methylcyclohexane and  $1.4 \times 10^{-3}$  mole % DMPD, the O.D. of DMPD<sup>+</sup> increases linearly for 1, 2, 3, and 4 mole % of added carbon tetrachloride. Unlike DMPD, TMPD is photooxidized in hydrocarbon glasses without promoters. Its yield is strongly promoted by bromoform or carbon tetrabromide, but not by carbon tetrachloride.

To determine whether photoionization involved 1 or 2 quanta, light intensity was varied fourfold keeping the integrated flux constant. The same cation yield was found in all runs using DMPD and carbon tetrachloride in M<sub>2</sub>P<sub>3</sub>. Thus photoionization (in Pyrex cells) involves the first excited singlet of DMPD since  $\lambda_{\max}$  for DMPD is 320 m $\mu$ . Our results do not distinguish between ionization of the singlet or triplet. For TMPD in 3MP, Meyer and Albrecht conclude that the vibrationally excited singlet state is responsible.

$\gamma$ -Irradiations at  $-196^\circ$ .—Irradiation of 1.0 mole % DMPD in MTHF produced an O.D. of 0.14 for DMPD<sup>+</sup> at 575 m $\mu$  or  $G(\text{cation}) = 0.27$ . The O.D. at 1200 m $\mu$  for solvated electrons was *ca.* 4.1 or  $G(\text{electrons}) = 2.6$ . Optical bleaching of the solvated electron band decreased the O.D.<sub>575</sub> to 0.05, apparently by charge recombination.

In a similar experiment with 5 mole % carbon tetrachloride also present in the glass, the O.D.<sub>575</sub> was 0.47, or  $G(\text{cation}) = 0.88$ . On warming, a green precipitate formed which dissolved in water to give the spectrum of DMPD<sup>+</sup>.

A solution of 0.01 mole % DMPD in MTHF was illuminated until O.D.<sub>575</sub> was 0.25; it was then  $\gamma$ -irradiated to a dose of  $2 \times 10^{18}$  e.v./g. Although a large yield of solvated electrons was produced, the O.D. remained the same, even upon bleaching of the electrons. Thus, most of the cations produced photochemically cannot react with electrons generated by  $\gamma$ -irradiation or released by photodetachment.

The solubility of DMPD in hydrocarbon glasses is small. Irradiation of  $7 \times 10^{-3}$  mole % DMPD in 3MP, or of 0.04 mole % DMPD in 2MP-1, produced no cation. Irradiation with carbon tetrachloride or 2-propyl chloride again yielded no cation.

Although TPA is not suitable for photooxidation, it is sufficiently soluble in the glasses used to permit studies using  $\gamma$ -irradiation. Irradiation of 0.53 mole % TPA in MTHF resulted in an O.D. of 0.22 at 640  $m\mu$  and very little formation of solvated electrons. A new absorption with  $\lambda_{\max} > 1600$   $m\mu$  appeared. Bleaching with the Corning No. 2600 filter decreased the O.D. at 640  $m\mu$  to 0.18. Irradiation of 0.13 mole % TPA in MTHF gave an O.D. of 0.04 at 640  $m\mu$ ; with 1 mole % carbon tetrachloride also present the O.D. was 0.16.

Irradiation of TPA in hydrocarbon glasses gave higher yields than in MTHF. Results appear in Table II. For both runs in 2MP-1 the alkene cation band did not appear. Without carbon tetrachloride, absorption is present with  $\lambda_{\max}$  at 1800  $m\mu$ , but this could be due either to the usual 2MP-1 electron band or to the TPA anion mentioned before. Bleaching this band removed the TPA cation band.

TABLE II  
YIELDS OF TRIPHENYLAMINE CATIONS IN HYDROCARBON GLASSES WITH ADDITIVES<sup>a</sup>

| Glass | Mole % additive                         | O.D. <sub>640 <math>m\mu</math></sub> |
|-------|---|---------------------------------------|
| 3MP   | None                                    | 0.32                                  |
| 3MP   | 1.4 CH <sub>2</sub> CHClCH <sub>3</sub> | 0.73                                  |
| 3MP   | 1.3 CCl <sub>4</sub>                    | 0.83                                  |
| 3MP   | 12 CCl <sub>4</sub>                     | 1.4                                   |
| 2MP-1 | None                                    | 0.24                                  |
| 2MP-1 | 1.0 CCl <sub>4</sub>                    | 0.71                                  |

<sup>a</sup> 0.1 mole % TPA and  $6.5 \times 10^{18}$  e.v./g. for all runs.

Many experiments performed with samples exposed to air support the observation that yields of amine cation from  $\gamma$ -irradiation are smaller in polar than in nonpolar glasses. Irradiation of 0.2 mole % TPA in M<sub>2</sub>P<sub>3</sub> gave an O.D. of 0.68 at 640  $m\mu$ ; for 0.6 mole % TPA in EPA the O.D. was 0.47. Addition of 14 mole % carbon tetrachloride to 0.2 mole % TPA in M<sub>2</sub>P<sub>3</sub> enhanced the O.D. to 1.50.

Irradiation of 0.066 mole % DMPD in air saturated EPT glass gave  $G(\text{DMPD}^+) \cong 1.86$ , which increased to  $G(\text{DMPD}^+) \cong 4$  with 10 mole % carbon tetrachloride using the extinction coefficient measured in aqueous solution. Using the extinction coefficient for TMPD<sup>+</sup> in 3MP at  $-196^\circ$ ,<sup>7</sup> irradiation of  $5 \times 10^{-3}$  mole % TMPD in EPT gave  $G(\text{TMPD}^+) = 0.35$ ; with 15 mole % bromoform present the yield of cation was 0.96.

Experiments with MDPA in air gave similar results. Irradiation of 0.2 mole % MDPA in M<sub>2</sub>P<sub>3</sub> gave an O.D. of 0.83 at 650  $m\mu$ , which increased to 1.09 with 10 mole % carbon tetrachloride. By contrast, 2.6 mole % MDPA in EPA gave an O.D. of only 0.62, and 0.66

mole % MDPA in EPA gave an O.D. of 0.31. These results confirm smaller yields in polar glasses.

**Photolyses at Room Temperature.**—Photolysis of  $10^{-2}$  mole % DMPD in air-free isopentane gave no colored product nor did subsequent extraction with water. When photolysis was conducted in aerated isopentane solution, absorption bands appear at 510, 450, and 390  $m\mu$ . The aqueous extract shows the cation bands at 510 and 550  $m\mu$ . Photolysis of isopentane solutions containing carbon tetrachloride, methyl iodide, propyl bromide, ethyl bromide, or phenyl bromide all yield green precipitates. In each case the aqueous solution of this salt exhibits the DMPD<sup>+</sup> spectrum.

Photolysis of the dihydrochloride of DMPD in water (pH  $\sim 5$ ) yields Wurster's red. This product decays slowly in the dark by an approximately second-order rate process, as does chemically prepared DMPD<sup>+</sup>, but reliable spectral measurements can be made during the first few minutes.

The quantum yield of photooxidation of DMPD dihydrochloride in water was measured in a Pyrex cell with an AH-6 lamp and a Jena No. 313 filter providing light in the 320  $m\mu$  region, based upon ferrioxalate actinometry.<sup>9</sup> The quantum yield was *ca.* 0.06. Using a 2537 Å. resonance lamp in a Vycor cell the quantum yield was *ca.* 0.5.

Photolysis of aqueous solutions of DMPD at pH  $\sim 1$  by illumination in the first absorption band yields no colored product, but upon subsequent adjustment to pH  $\sim 5$  the spectrum of Wurster's red appears.

Subsequent to photolyses of air-free aqueous solutions of DMPD at pH  $\sim 5$  painstaking efforts to collect and mass analyze hydrogen were made repeatedly, but without success. If H-atoms are released by reduction of water, they must react by addition to the amine very efficiently since formation of 1% as much H<sub>2</sub> as DMPD<sup>+</sup> could have been detected.

To test for H-atom scavenging by amine,  $10^{-5}$  mole of DMPD·2HCl was photolyzed in 5 ml. of D<sub>2</sub>O *in vacuo* at 320  $m\mu$  to form  $0.8 \times 10^{-6}$  mole of DMPD<sup>+</sup>. The solvent was removed and the same amount of water added and removed twice by distillation to remove exchangeable deuterium. Air was admitted to the dry residue which was heated until substantially complete oxidation occurred. The combustion products were distilled onto sodium on the vacuum line yielding  $29 \times 10^{-6}$  mole of hydrogen which contained  $0.42 \times 10^{-6}$  mole of HD by mass analysis. This analysis cannot be considered fully quantitative, but the ratio  $(0.42 \times 10^{-6} \text{ mole of HD}) / (0.8 \times 10^{-6} \text{ mole of DMPD}^+)$  provides qualitative evidence for incorporation of hydrogen into the aromatic ring.

**$\gamma$ -Irradiations at *ca.* 20°.**—Air-free solutions of DMPD in 3MP at laboratory temperature yielded no DMPD<sup>+</sup> by radiolysis. With carbon tetrachloride also present a green precipitate formed which gave the spectrum of DMPD<sup>+</sup> in aqueous solution. Other experiments were performed with radiolysis yields measured optically following extraction into water. Using *ca.* 5 mole % DMPD in 3MP with *ca.* 20 mole % halide added, it was found that chloroform, ethylene dibromide, bromoform, and carbon tetrabromide promoted formation of DMPD<sup>+</sup> with *G*-values of the order

(9) C. A. Parker, *Proc. Roy. Soc. (London)*, **A235**, 518 (1956).

of unity; but bromobenzene, methyl iodide, and trityl chloride did not. Results were qualitatively similar with 0.2 mole % DMPD in isopentane.

### Discussion

Simple photoionization of DMPD by absorption of a quantum in the 320 m $\mu$  region in hydrocarbon solvents, or even in polar media, cannot be reconciled with plausible energetics. It is quite clear, however, that ion pairs are produced under selected conditions when an appropriate electron acceptor is present and both ionic species can be detected. This was demonstrated by using biphenyl and benzophenone as electron acceptors since the spectra of their anions are known. For the organic halides electron transfer leads to dissociation as demonstrated by the appearance of benzyl radical absorption when benzyl chloride served as electron acceptor. The same effect has been observed in  $\gamma$ -irradiated glasses.<sup>2,3</sup> As an example, for carbon tetrachloride  $D_{C-Cl} = 3.30$  e.v.<sup>10</sup> while the electron affinity is 3.78 e.v.<sup>11</sup> In a nonpolar medium the polarization energy of e<sup>-</sup> and Cl<sup>-</sup> cancel leaving a net 0.48 e.v. Polarization energy of the amine cation in a hydrocarbon environment may be 1–2 e.v. Excitation of the amine by light contributes about 4.1 e.v. Ionization potentials of these amines are not known and may be estimated to be 7.5 e.v. The energy imbalance of 1–2 e.v. applies to infinitely separated ions. In rigid, low dielectric media the yield of photooxidized amine is still increasing with 10% electron acceptor, implying nearest neighbor interaction. At such small charge separation the coulombic energy is less than 2 e.v. and the net process of ion pair formation is quite plausibly exothermic. Since no great charge separation can be accounted for in the act of ion-pair formation it is probable that the electron acceptor interacts with the electronically excited amine. This mechanism is supported by the fact that organic halides did not exhibit a gradual change in effectiveness as electron acceptors, but either did or did not promote oxidation. This is very unlike the behavior of organic halides in trapping electrons in  $\gamma$ -irradiated glasses where changes are gradual, not discontinuous. Also, biphenyl attaches electrons in both polar and nonpolar  $\gamma$ -irradiated glasses.

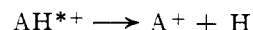
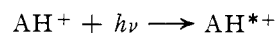
In low dielectric media the irreversibility of photooxidation clearly requires formation of a very stable anion, *e.g.*, a halide. Biphenyl and other molecular electron acceptors have insufficient electron affinity for the purpose and reversion to reactants readily occurs, even in the glassed hydrocarbon. In MTHF glass, however, the biphenylide ion is stabilized by ion-permanent dipole interaction.

In aqueous medium a possible mechanism for the photooxidation of an amine hydrochloride (AH<sup>+</sup>) would be loss of H from the protonated amino group

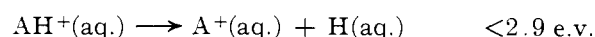
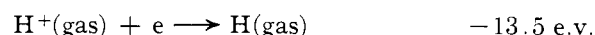
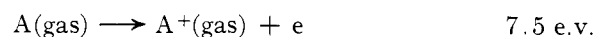
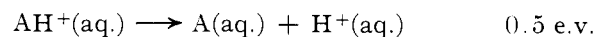
(10) R. E. Fox and R. K. Curran, *J. Chem. Phys.*, **34**, 1595 (1961).

(11) F. M. Page, *Advances in Chemistry Series*, No. 36, American Chemical Society, Washington, D. C., 1962, p. 68.

of the excited ion



The relevant thermochemistry can be estimated:



The most striking difference between photo- and  $\gamma$ -induced oxidation of amines is the relatively much smaller yield in hydrocarbon than in polar media of  $\gamma$ -irradiated samples. Thus  $G(TPA^+)$  in MTHF is about 6% of the yield in 3MP. It also appears significant that 2-propyl chloride promotes yields of amine cation in radiolysis but not in photolysis. Since this reagent is known to attach electrons in  $\gamma$ -irradiated glasses, it appears that the mechanism for promoting the yield of amine cations may also involve the same electron attachment. The positive hole, so stabilized, can then migrate to the amine. An alternate proposal would be formation of more highly excited states of the amine which can react with less efficient electron acceptors. Only the first of these possibilities is consistent with the inhibiting effect of polar solvents upon cation yields from  $\gamma$ -irradiation. In the mass spectrometer<sup>12</sup> proton transfer to polar molecules has been observed for amines, alcohols, ethers, etc. In organic glasses at  $-196^\circ$ , color centers attributed to various solute cations have been observed in hydrocarbon media. Their yields are invariably depressed by adding only 1–5% of ether, alcohol, or amine.<sup>13,14</sup>

**The Samuel–Magee Theory.**—Optical bleaching of solvated electrons was shown to remove substantially all DMPD<sup>+</sup> produced by radiolysis in MTHF or in 20% MTHF + 80% 3MP. Similar effects have often been observed for other cations. When DMPD<sup>+</sup> was first produced in MTHF by photolysis, subsequent radiolysis had no effect upon this absorption, neither did optical bleaching of the electron band then diminish DMPD<sup>+</sup> absorption.

It must be concluded that ion pairs produced by  $\gamma$ -irradiation recombine only with each other, as proposed originally by Samuel and Magee.<sup>15</sup>

(12) T. F. Moran and W. H. Hamill, *J. Chem. Phys.*, **39**, 1413 (1963).

(13) W. H. Hamill, J. P. Guarino, M. R. Ronayne, and J. A. Ward, *Discussions Faraday Soc.*, in press.

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(15) A. H. Samuel and J. L. Magee, *J. Chem. Phys.*, **21**, 1080 (1953).